# REPORT DOCUMENTATION PAGE Dist. A

Form Approved
OMB No. 0704-0188



| 1. AGENCY USE ONLY (Leave blank) | 2. REPORT DATE | 3. REPORT TYPE AND DATES COVERED |
|---|---|---|
| | | FINAL 01 Sep 92 TO 30 Nov 94 |

**4. TITLE AND SUBTITLE**

CONJUGATED POLYMERS FROM CYCLOHEXADIENEDIOL MONOMERS

**5. FUNDING NUMBERS**

F49620-92-J-0483
61102F
2303/DS

**6. AUTHOR(S)**

Dr Robert H. Grubbs

**7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)**

Dept of Chemistry
California Institute of Technology
Pasadena CA 91125

**8. PERFORMING ORGANIZATION REPORT NUMBER**

AFOSR-TR- 95 0004

**9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)**

AFOSR/NL
110 Duncan Ave Suite B115
Bolling AFB DC 20332-0001
Dr Frederick L. Hedberg

**10. SPONSORING/MONITORING AGENCY REPORT NUMBER**



**11. SUPPLEMENTARY NOTES**

**12a. DISTRIBUTION/AVAILABILITY STATEMENT**

Approved for public release; distribution unlimited.

**12b. DISTRIBUTION CODE**

A

**13. ABSTRACT** (Maximum 200 words)

The ICI cyclohexadiene monomer has been used to prepare poly(arylenevinylene) derivatives through a precursor route. The polyarylene vinylenes show interesting properties and some derivatives have been used to fabricate photoemitting diodes. A general route to polynathphalene vinylenes has been developed that is now being expanded in to the synthesis of block polymers. A simple route to substituted benzyne precursors (8a,b) was developed and the resulting benzynes were added to the ICI monomer. It was found that these adducts (9a,b) would not ROMP with any of the available catalysts.



| 14. SUBJECT TERMS | | | 15. NUMBER OF PAGES |
|---|---|---|---|
| | | | 16. PRICE CODE |
| 17. SECURITY CLASSIFICATION OF REPORT | 18. SECURITY CLASSIFICATION OF THIS PAGE | 19. SECURITY CLASSIFICATION OF ABSTRACT | 20. LIMITATION OF ABSTRACT |
| (U) | (U) | (U) | (U) |

AFOSR, F49620-92-J-0483

Program Manager: Frederick L. Hedberg ~~NC~~ NL

September 1, 1992 - November 30, 1995

Robert H. Grubbs
Division of Chemistry and Chemical Engineering
California Institute of Technology
Pasadena, CA 91125

Final
~~Technical~~ Report
January 31, 1995

"Conjugated Polymers from Cyclohexadienediol Monomers"
Reporting Period: 9/1/93 - 11/30/94

**Robert H. Grubbs**
**California**
**Institute of Technology**
**Pasadena, California 91125**

**Technical Report**

# Conjugated Polymers From Cyclohexadienediol Monomers

Technical Report

a. Publications

"New Syntheses of Benzobarrelenes." L. Pu and R. H. Grubbs, *J. Org.Chem.* **1994**, *59*, 1351-1353.

"Stereoregular Precursors to Poly(*p*-phenylene) via Transition-Metal-Catalyzed Polymerization. 1. Precursor Design and Synthesis." D. L. Gin, V. P. Conticello, and R. H. Grubbs, *J. Am. Chem. Soc.* **1994**, *116*, 10507-10519.

"Stereoregular Precursors to Poly(*p*-phenylene) via Transition-Metal-Catalyzed Polymerization. 2. The Effects of Polymer Stereochemistry and Acid Catalysts on PrecursorAromatization." D. L. Gin, V. P. Conticello, and R. H. Grubbs, *J. Am. Chem. Soc.* **1994**, *116*, 10934-10947.

"Routes to Conjugated Polymers with Ferrocenes in their Backbones: Synthesis and Characterization of Poly(ferrocenylene divinylene) and Poly(ferrocenylene butenylene)." C. E. Stanton, T. R. Lee, R. H. Grubbs, N. S. Lewis, J. K. Pudelski, M. R. Callstrom, M. S. Erickson, M. L. McLaughlin, *J. Am. Chem. Soc.*, submitted.

"Poly-(1,4-Naphthalene Vinylenes): Synthesis of a New Class of Soluble Conducting Polymers." L. Pu, M. W. Wagaman, and R. H. Grubbs, *Macromolecules*, submitted.

"Highly Unsaturated Oligomeric Hydrocarbons: a-(Phenylethynyl)-w-phenylpoly[1,2-phenylene(2,1-ethynediyl)]." R. H. Grubbs and D. Kratz, *Chem. Ber.* **1993**, *126*, 149-157.

"The Optical and Electrical Properties of New Types of Poly(Arylenevinylenes)" G. Leising, L. Pu, M. W. Wagaman, and R. H. Grubbs, in preparation.

b. Chapters

"Ring -Chain Equilibria in Ring-Opening Metathesis Polymerization (ROMP) of Cycloolefins" Zhongren Chen, J. A. Kornfield, J.P. Claverie, R.H. Grubbs, *Polymer Preprints*, **1994,** 692

c. Graduate students supported

J.P. Claverie

M. Wagaman

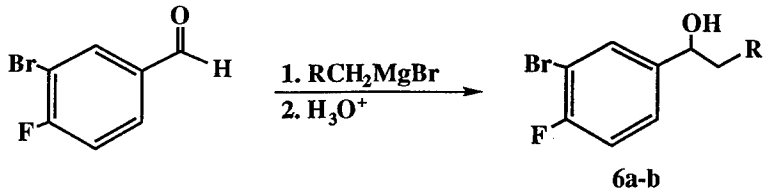
d. Postdoctorals Supported

Lin Pu

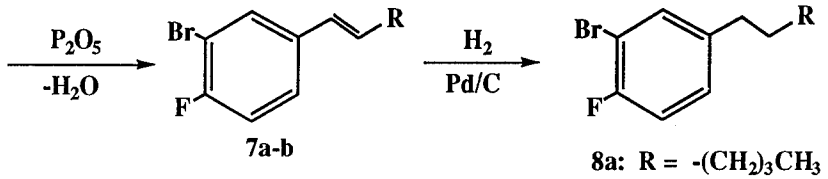
Technical Accomplishments:

**Polyarylenevinylene:**

The ICI cyclohexadiene monomer has been used to prepare poly(arylenevinylene) derivatives through a precursor route. The polyarylene vinylenes show interesting properties and some derivatives have been used to fabricate photoemitting diodes. A general route to polynathphalene vinylenes has been developed that is now being expanded in to the synthesis of block polymers. A simple route to substituted benzyne precursors (**8a,b**) was developed and the resulting benzynes were added to the ICI monomer. It was found that these adducts (**9a,b**) would not ROMP with any of the available catalysts.



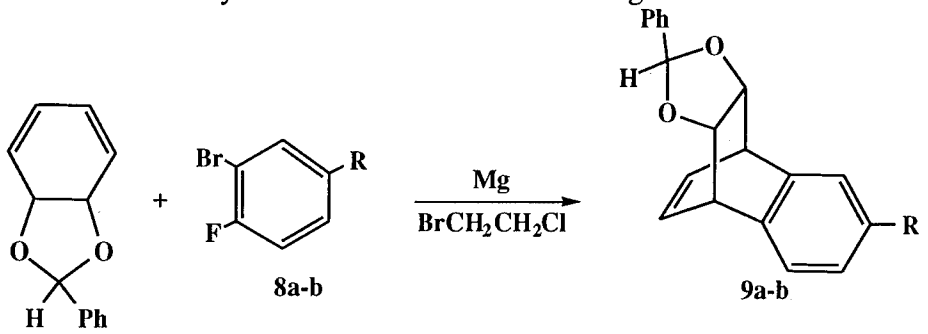

6a-b




7a-b

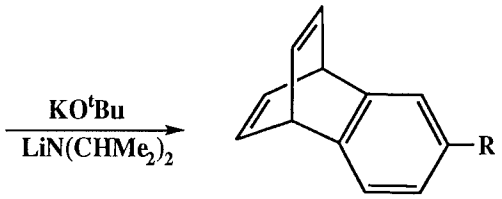
8a: R = $-(CH_2)_3CH_3$
8b: R = $-(CH_2)_8CH_3$

However the adducts could be converted to benzobarrelene analogs (**10a,b**) by the treatment of the benzaldehyde acetal derivative with a strong base such as LDA.



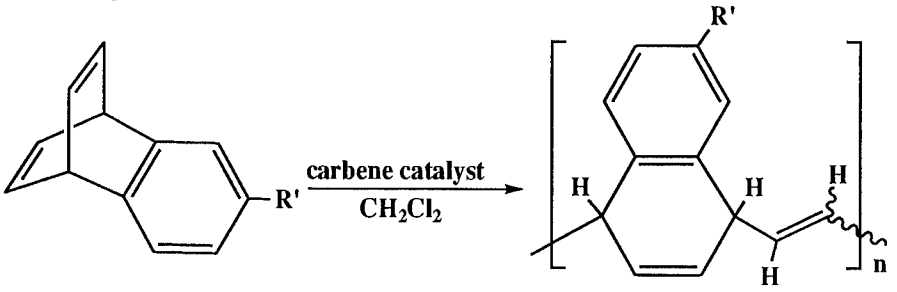

8a-b

9a-b




10a: R = $-(CH_2)_3CH_3$
10b: R = $-(CH_2)_8CH_3$

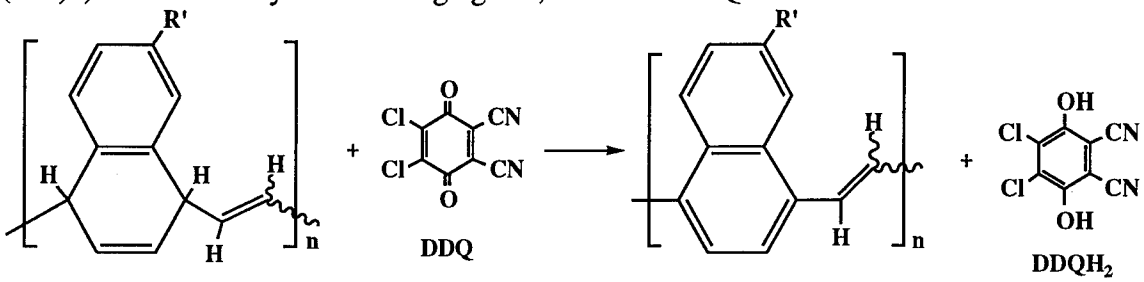
The resulting benzobarrelenes could be polymerized to **11a ,b** in high yields with a variety of ROMP catalysts. These living systems could be used to control the molecular weight and molecular weight distribution.




10a-b

11a: R' = $-(CH_2)_4CH_3$
11b: R' = $-(CH_2)_{10}CH_3$

The resulting soluble polymers could then converted to the soluble vinylenenaphthylene **(13a,b)** with a variety of oxidizing agents, however DDQ was the most effective.




**11a-b**

**13a: R' = -$(CH_2)_4CH_3$**
**13b: R' = -$(CH_2)_{10}CH_3$**

The UV/Vis spectrum of **13a** displays a strong absorbance at 448 nm, which demonstrates the formation of an extended p-conjugation in the oxidized polymer after the dehydrogenation of **11a** (Figure 1 & 2). The UV/Vis spectrum of **13b** shows a similar absorbance at 450 nm. When excited at 440 nm, the fluorescence emission spectra of **13a** and **13b** show strong signals at 583 nm and 572 nm respectively. By visual observation, solutions of the conjugated polymers glow yellow orange under UV irradiation. In preliminary studies, electroluminescence devices have been fabricated by spin coating using these materials. A key finding was that good internal electroluminescence quantum efficiencies of up to 0.05% could be obtained using an air stable Aluminum electrode. Derivatives that contain halogens as electron withdrawing groups have been prepared and converted to polymers. It has been found that these derivatives can be used to tune the emission spectrum of the resulting polymer.

Since the monomers that are being prepared are new substrates for ROMP, a method of predicting which compounds will polymerize has been developed and is being applied to a number of new substrates.

**Polyparaphenylene:** The final papers on the synthesis of polyparaphenylene have been published. A collaboration with A. MacDiarmid at U. of Penn has resulted in the conversion of the precursors into extremely stable films of PPP. Samples of the high molecular weight, linear precursor to polyparaphenylene that was prepared were sent to the University of Dayton, Edwards Airforce Base and to other federal laboratories. Other applications in the construction of blue electroluminesence diodes and in the development of a high density battery are being explored.